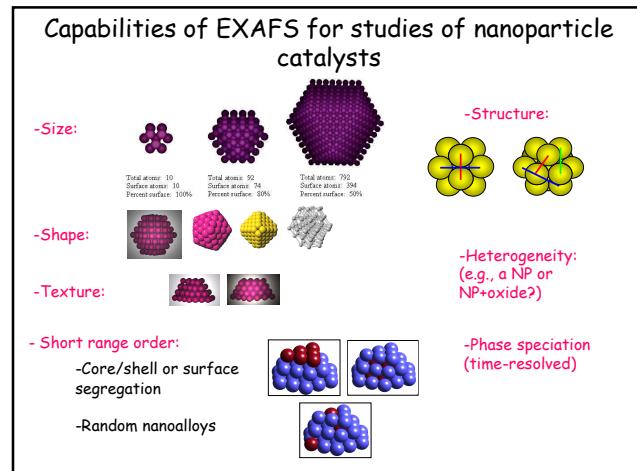


Application of XAFS to Nanocatalysis Science

Selected Topics in EXAFS Data Analysis

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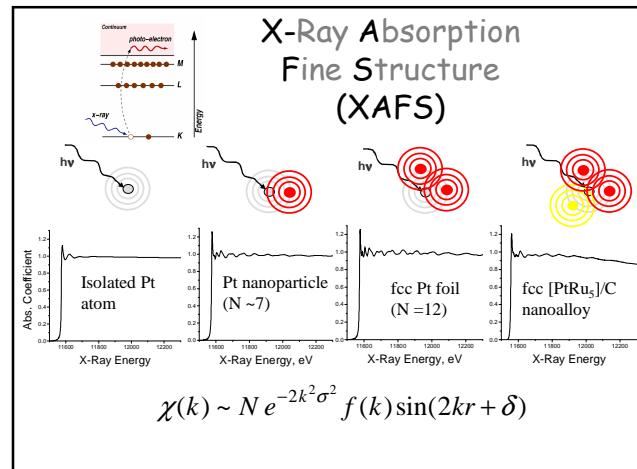


Phase speciation problem:

$$\mu = \sum_{i=1}^N x_i \mu(P_i)$$

Heterogeneous mixture

Can be solved with [principal component analysis \(PCA\)](#)



Theoretical EXAFS Equation:

Single scattering path:

$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} |f^{\text{eff}}(k)| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin[2kR - \frac{4}{3}C_3 k^3 + \delta(k)]$$

Multiple-scattering path:

$$\chi_{\Gamma}(k) = \text{Im } NS_0^2 \frac{e^{i \left(\sum_i R_{ii+} + 2\delta(k) \right)}}{\prod_i k R_{ii+}} e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \text{Tr } M F^N \cdots F^2 F^1$$

Theoretical EXAFS signal:

$$\chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k)$$

Definition of Parameter Space:

In IFEFFIT, parametrization is the same for SS and MS paths:

$$k = \sqrt{\frac{2m}{\hbar^2} (E - E_0)} \quad R = R_{\text{model}} + \Delta R$$

$$E_0 = E_0^{\text{bg}} + \Delta E_0$$

$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} |f^{\text{eff}}(k)| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin[2kR - \frac{4}{3}C_3 k^3 + \delta(k)]$$

Amplitude

FEFF

Fitting of EXAFS Theory to the Data:

$$f(R_i) = \tilde{\chi}(R_i) - \tilde{\chi}_M(R_i)$$

$$\chi_{\nu}^2 = \frac{1}{V} \sum_{i=1}^{N_{\text{idp}}} \left(\frac{f_i}{\epsilon_i} \right)^2 = \frac{N_{\text{idp}}}{NV} \sum_{i=1}^N \left(\frac{f_i}{\epsilon_i} \right)^2$$

$$\nu = N_{\text{idp}} - P \quad (\text{Number of degrees of freedom})$$

$$N_{\text{idp}} = \frac{2\Delta k \Delta R}{\pi} \quad (\text{Number of relevant independent data points})$$

E. A. Stern
Phys. Rev. B **48**, 9825-9827 (1993)

$$\chi_{\nu}^2 = \frac{1}{V} \sum_{i=1}^{N_{\text{idp}}} \left(\frac{f_i}{\epsilon_i} \right)^2 = \frac{N_{\text{idp}}}{NV\epsilon^2} \sum_{i=1}^N [\text{Re}(f_i)^2 + \text{Im}(f_i)^2]$$

FEFF Fitting and Error Analysis

Remove background: $\mu(E) \rightarrow \chi(k)$

AUTOBK algorithm: M. Newville, P. Livins, Y. Yacoby, E. A. Stern, and J. J. Rehr, Phys. Rev. B **47**, 14126-14131 (1993).

Fourier transform data: $\chi(k) \rightarrow \tilde{\chi}(r)$

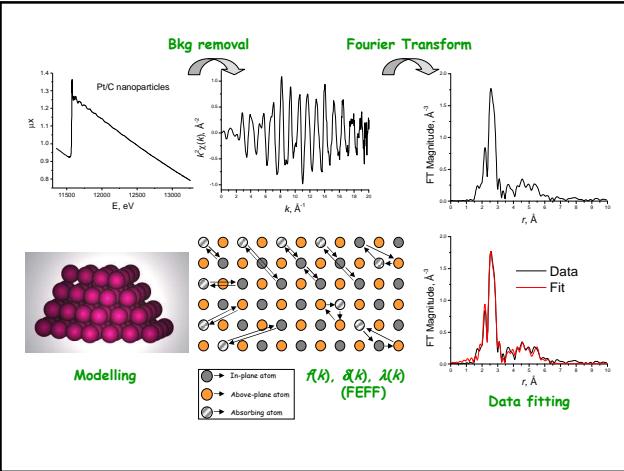
Pick a model

Calculate $f(k)$, $\delta(k)$ and $\lambda(k)$: FEFF

FEFF review: J.J. Rehr & R.C. Albers, Rev. Mod. Phys. (2000) 72, 621-654

Fit theory to data

Error analysis $\{x_i \pm \delta x_i\}$



Different approaches toward obtaining cluster size from n_1 ...

1. Analytical approach

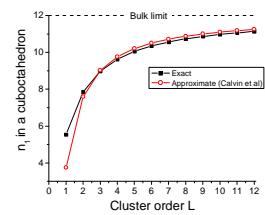
$$n_1^{\text{co}} = \frac{24L(5L^2 + 3L + 1)}{10L^3 + 15L^2 + 11L + 3}$$

Montejano-Carrizales, et al, Nanostruct. Mater. **8**, 269 (1997)

$$n_1 \approx \left[1 - \frac{3}{4} \left(\frac{r}{R} \right) + \frac{1}{16} \left(\frac{r}{R} \right)^3 \right] n_1^{\text{bulk}}$$

S. Calvin, et al, JAP **778**, 94 (2003)

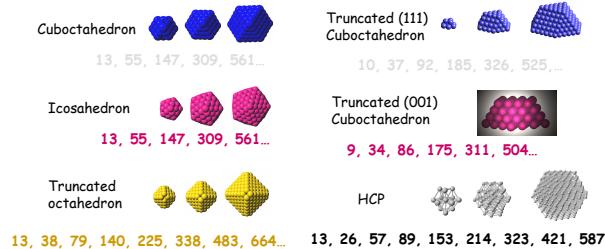
$$n_1^{\text{icos}} = \frac{6L(20L^2 + 15L + 7)}{10L^3 + 15L^2 + 11L + 3}$$



2. Numerical approach

2.1 Generating cluster geometry

Glasner, Frenkel, AIP Conf. Proc. **882**, 746-748 (2007).



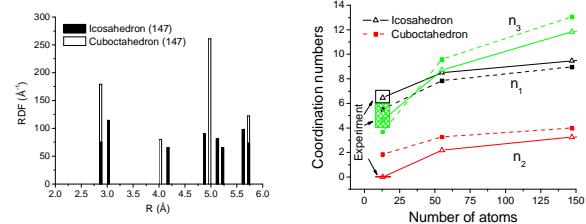
<http://www.yu.edu/scc>

2.2 Calculating radial distribution function and coord. numbers

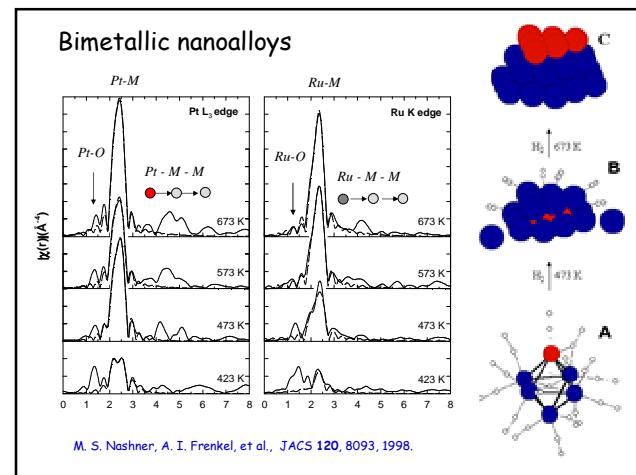
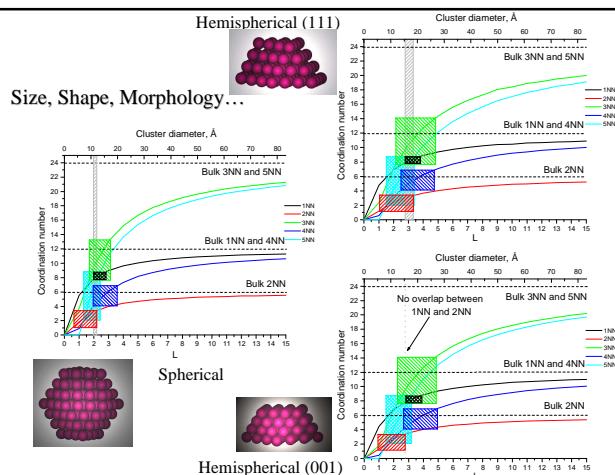
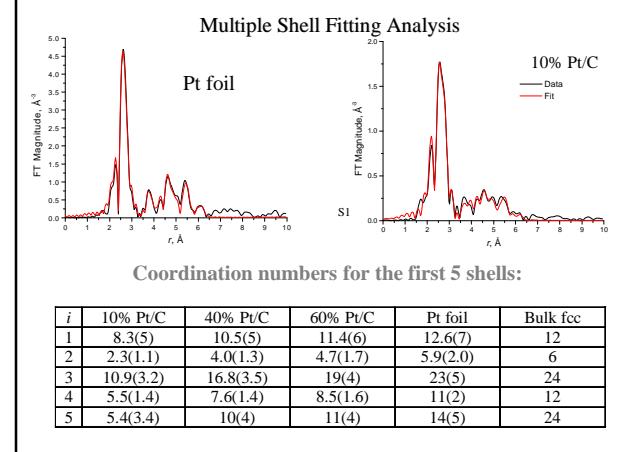
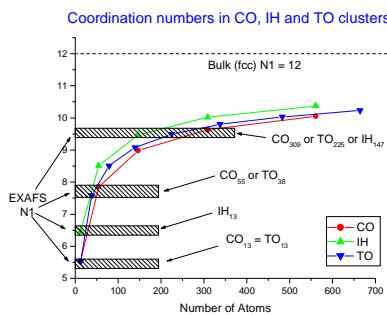
$$\rho(r) = \frac{1}{N} \sum_{i=1}^N \rho_i(r)$$

$$\rho_i(r) = \frac{dN_i}{dR_i}$$

$$n_i = \int_{R_1}^{R_2} \rho(r) dr$$



First shell analysis is not adequate for full structural studies of small clusters



Short range order in bimetallic nanoparticles

Random alloys: $\frac{n_{AA}}{n_{AB}} = \frac{x_A}{x_B}$

Short range order in nanoalloys: $\alpha = 1 - \frac{n_{AB}/n_{AM}}{x_B}$

$$n_{AM} = n_{AA} + n_{AB}$$

$\frac{n_{AA}}{n_{AB}} > \frac{x_A}{x_B}$ $\alpha > 0$ Positive tendency to clustering

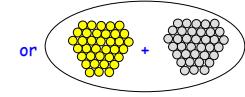
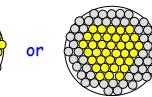
$\frac{n_{AA}}{n_{AB}} < \frac{x_A}{x_B}$ $\alpha < 0$ Negative tendency to clustering

$\frac{n_{AA}}{n_{AB}} = \frac{x_A}{x_B}$ $\alpha = 0$ Random alloy

Are the elements alloyed?

If yes, are they mixed randomly?

If not, can we identify any pattern (e.g., a core/shell)?



Random

Intra-particle
segregation

Inter-particle
segregation

$$\frac{n_{AA}}{n_{AB}} = \frac{x_A}{x_B}$$

$$n_{AM} < n_{BM}$$

$$n_{AB} = 0$$

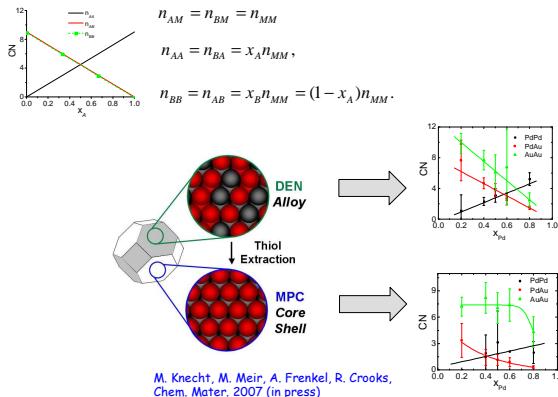
B-rich core/A-rich shell

Can be independently
obtained by EDS

Size determination: $n_{MM} = x_A n_{AM} + x_B n_{BM}$

A.Frenkel, Z. Kristallogr. 2007 (in press)

Random alloys:



Heterogeneity and EXAFS

$$\rho(r) = \sum_{s=1}^n x_s \rho^{(s)}(r) \quad x_s = \frac{N_s}{N} \quad \sum_{s=1}^n x_s = 1$$

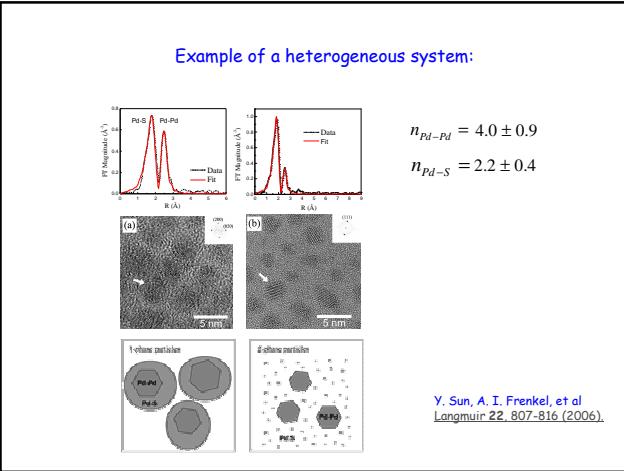
$$n_{ME_i} = x_s \frac{N_{ME_i}}{N_s} = x_s n_{ME_i}^{(s)} \quad E_i \neq M$$

$$n_{MM} = x_s \frac{2N_{MM}}{N_s} = x_s n_{MM}^{(s)} \quad E_i = M$$

Homogeneous system: $N_s = N$ $x_s = 1$ $n_{ME_i} = n_{ME_i}^{(s)}$

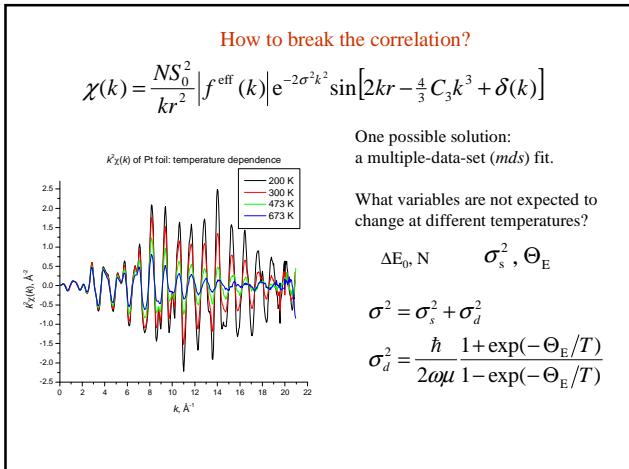
Heterogeneous mixture: $N_s < N$ $x_s < 1$ $n_{ME_i} < n_{ME_i}^{(s)}$

Thus, the size of the particles will be **underestimated** if heterogeneity is present but ignored in analysis



Some technical details:

Multiple edge analysis: $n_{AB} = \frac{x_B}{x_A} n_{BA}$
 $R_{AB} = R_{BA}$
 $\sigma_{AB}^2 = \sigma_{BA}^2$



Debye Waller Factors of Collinear Multiple-Scattering Paths

$$\vec{r}_{ii+} = \vec{R}_{ii+} + \vec{u}_{i+} - \vec{u}_i$$

Notation:
A.V.Potarkova and J.J. Rehr,
Phys. Rev. B 59, 948 (1999).

$$r_{ii+}^2 = (\vec{R}_{ii+} + (\vec{u}_{i+} - \vec{u}_i))^2 \approx R_{ii+}^2 - 2R_{ii+}\hat{R}_{ii+}(\vec{u}_i - \vec{u}_{i+})$$

$$r_{ii+} = R_{ii+}\sqrt{1 - 2\frac{\hat{R}_{ii+}}{R_{ii+}}(\vec{u}_i - \vec{u}_{i+})} \approx R_{ii+}\left(1 + \frac{\hat{R}_{ii+}}{R_{ii+}}(\vec{u}_i - \vec{u}_{i+})\right) = R_{ii+} + (\vec{u}_i - \vec{u}_{i+})\hat{R}_{ii+}$$

$$r_j \equiv \frac{1}{2} \sum_{i=1}^{n_j} r_{ii+} = R_j + \frac{1}{2} \sum_{i=1}^{n_j} (\vec{u}_i - \vec{u}_{i+})\hat{R}_{ii+}$$

$$R_j \equiv \frac{1}{2} \sum_{i=1}^{n_j} R_{ii+}$$

$$\sigma_j^2 \equiv \left\langle (r_j - R_j)^2 \right\rangle = \left\langle \left(\frac{1}{2} \sum_{i=1}^{n_s} (\bar{u}_i - \bar{u}_{i+}) \hat{R}_{ii+} \right)^2 \right\rangle = \frac{1}{4} \left\langle \left(\sum_{i=1}^{n_s} (\bar{u}_i - \bar{u}_{i+}) \hat{R}_{ii+} \right)^2 \right\rangle$$

$\sigma_{ss}^2 = \frac{1}{4} \left\langle [(\bar{u}_a - \bar{u}_c) \hat{R}_0 + (\bar{u}_c - \bar{u}_a) (-\hat{R}_0)]^2 \right\rangle = \frac{1}{4} \left\langle [2(\bar{u}_a - \bar{u}_c) \hat{R}_0]^2 \right\rangle$
 $= \left\langle [\bar{u}_a \hat{R}_0]^2 \right\rangle + \left\langle [\bar{u}_c \hat{R}_0]^2 \right\rangle - 2 \left\langle [\bar{u}_a \hat{R}_0] [\bar{u}_c \hat{R}_0] \right\rangle$
 $= \langle u_{ax}^2 \rangle + \langle u_{cx}^2 \rangle - 2 \langle u_{ax} u_{cx} \rangle,$
 $\hat{R}_{ab} = \hat{R}_{bc} = -\hat{R}_{ca} \equiv \hat{R}_0$
 $\sigma_{ds}^2 = \frac{1}{4} \left\langle [(\bar{u}_a - \bar{u}_b) \hat{R}_0 + (\bar{u}_b - \bar{u}_c) \hat{R}_0 + (\bar{u}_c - \bar{u}_a) (-\hat{R}_0)]^2 \right\rangle$
 $= \frac{1}{4} \left\langle [2(\bar{u}_a - \bar{u}_c) \hat{R}_0]^2 \right\rangle = \left\langle [\bar{u}_a \hat{R}_0]^2 \right\rangle = \sigma_{ss}^2$
 $\sigma_{ts}^2 = \sigma_{ds}^2 = \sigma_{ss}^2$

$$\sigma_{ss1}^2 = \left\langle u_{ax}^2 \right\rangle + \left\langle u_{cx}^2 \right\rangle - 2 \langle u_{ax} u_{cx} \rangle,$$

$\sigma_{ds}^2 = \frac{1}{4} \left\langle [(\bar{u}_a - \bar{u}_c) \hat{R}_0 + (\bar{u}_c - \bar{u}_b) (-\hat{R}_0) + (\bar{u}_b - \bar{u}_a) \hat{R}_0]^2 \right\rangle$
 $= \frac{1}{4} \left\langle [2(\bar{u}_b - \bar{u}_c) \hat{R}_0]^2 \right\rangle = \left\langle [\bar{u}_b \hat{R}_0]^2 \right\rangle + \left\langle [\bar{u}_c \hat{R}_0]^2 \right\rangle - 2 \langle u_{bx} u_{cx} \rangle$
 $= 2 \langle u_{bx}^2 \rangle - 2 \langle u_{bx} u_{cx} \rangle = \sigma_{ts}^2$
 $\sigma_{ts}^2 = \frac{1}{4} \left\langle 2[(\bar{u}_a - \bar{u}_c) \hat{R}_0 + 2(\bar{u}_c - \bar{u}_a) (-\hat{R}_0)]^2 \right\rangle$
 $= \frac{1}{4} \left\langle [4(\bar{u}_a - \bar{u}_c) \hat{R}_0]^2 \right\rangle = 4 \left\langle [\bar{u}_a \hat{R}_0]^2 \right\rangle = 4 \langle u_{ax}^2 \rangle + \langle u_{cx}^2 \rangle - 2 \langle u_{ax} u_{cx} \rangle = 4 \sigma_{ss1}^2$

P. Shanthakumar, M. Balasubramanian, D. Pease, A. I. Frenkel, D. Potrepka, J. Budnick, W. A. Hines, V. Kraizman Physical Review B 74, 174103 (2006).

